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TITLE OF INVENTION : Stretched Film

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No mention of crosslinking and E-beam.

Abstract

[Object] To provide a stretched film with excellent transparency, low temperature shrinking property, elastic recovery, and having improved tensile strength at fructure and elastic recovery ratio.

[Constitution] The film stock made of a cycloolefin copolymer containing a repeating unit derived from α-olefin and a repeating unit derived from cycloolefin and having a glass transition temperature (Tg) of lower than 30°C, is stretched monoaxially or biaxially to form a stretched film.

Claims

[Claim 1] Stretched film, prepared by stretching monoaxially or biaxially the film stock made of a cycloolefin copolymer containing a repeating unit derived from α-olefin and a repeating unit derived from cycloolefin and having a glass transition temperature (Tg) of lower than 30°C.

[Claim 2] The stretched film according to Claim 1, where the content of repeating unit derived from cycloolefin in the cycloolefin copolymer is 0.5 - 20 weight %.

Comprehensive explanation of invention

[0001]

[Field of commercial utility]

This invention relates to a stretched film that has excellent transparency, low temepraturе shrinking property and elastic recovery and can be used as the material for packing foods or as a material that can be used to pack a product for shipping.

[0002]

[Prior art and problems to be solved by the invention]

Monoaxially or diaxially drawn polyethylene and polypropylene films are used widely as the shrink film made of polyolefins. In this case, after the film is wire-cut and sealed, it is passed through a shrink tunnel while being exposed to infra-red heat, to shrink the film for packing. Therefore, the shrink film must have a low

temperature shrinking property so that heat will not cause a harmful effect on the content while it is passing through the shrink tunnel.

[0003]

Biaxially drawn sheet and film made of ethylene/cycloolefin copolymer is disclosed in Japanese Kokai Patent HEI 2-196832(1990) and Japanese Kokai Patent HEI 2-180976(1990). The copolymers disclosed in these Kokai Patent publications have a glass transition temperature in 50 - 230°C range and therefore they do not have acceptable low temperature shrinking property. This is obvious from the fact that the heat shrinkage ratio at 80°C is 0%. And, earlier the present inventors have proposed a thin molded article made of a copolymer prepared by copolymerizing α-olefin and cycloolefin at a certain ratio [Japanese Patent Application, HEI 3-99839(1991)]. This molded article, however, was not stretched, and its tensile fracture strength and elastic recovery was not always sufficient for certain applications.

[0004]

This invention was made in view of the above-described situation, and its object is to provide a stretched film that has excellent transparency, low temperature shrinking property and elastic recovery, and in addition has an improved tensile fracture strength and elastic recovery ratio.

[0005]

[Means to solve the problems]

As a result of an extensive investigation, the present inventors have discovered that the above-described object can be met effectively by using a cycloolefin copolymer having a certain glass transition temperature (Tg) and a certain structure as the feedstock to make the stretched film.

[0006]

Thus, this invention intends to provide a stretched film, as characterized by stretching, monoaxially or biaxially, a film stock made of cycloolefin copolymer containing a repeating unit derived from α-olefin and a repeating unit derived from cycloolefin, and having a glass transition temperature (Tg) of lower than 30°C.

[0007]

This invention is explained comprehensively below. The stretched film of this invention is made of a cycloolefin copolymer containing α-olefin unit and cycloolefin unit. Even though there is no particular restriction, those olefins containing a repeating unit represented by the following general formul [X] can be mentioned as the α-olefins.

[Chemical formula 1]

$$-(-CH_2-\underset{\displaystyle R^a}{\underset{|}{C}}H-)- \qquad \ldots[X]$$

[In the formula [X], R^a represents a hydrogen atom or a C_1 - C_{20} hydrocarbon group]

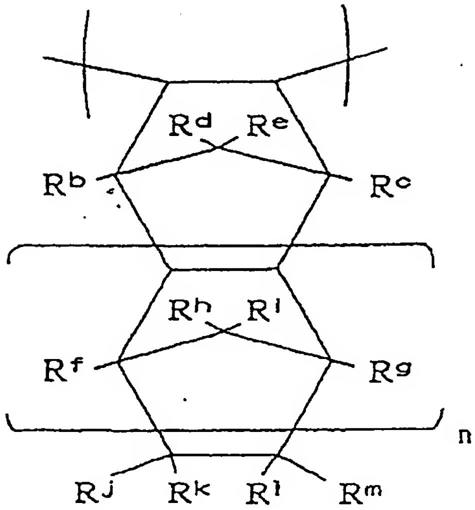
[0008]

In the repeating unit represented by the above general formula [X], R^a is a hydrogen atom or a C_1 - C_{20} hydrocarbon group. Examples of the hydrocarbon group having 1 - 20 carbons are methyl group, ethyl group, isopropyl group, isobutyl group, n-butyl group, n-hexyl group, octyl group and octadecyl group and so on. And, examples of the α-olefin to give the repeating unit represented by the general formula [X] are ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-hexene, 1-octene, decene, and eicocene and so on.

[0009]

And, even though there is no particular restriction, those which have the repeating units represented by the following general formula [Y] can be mentioned as the the cycloolefins.

[Chemical formula 2]



...[Y]

[in the formula (Y), R^b - R^m represent hydrogen atoms, hydrocarbon groups having 1 - 20 carbons, or substituting groups containing halogen atoms, oxygen atoms or nitrogen atoms, and n represents an integer of more than 0. R^j or R^k may form a ring with R^l or R^m. And, R^b - R^m may be mutually identical or different]

[0010]

In the repeating unit of the cycloolefin represented by the general formula [Y], R^b - R^m, as stated before, represents C_1 - C_{20} hydrocarbon groups or substituting groups containing halogen atom, oxygen atom or nitrogen atom. Examples of the C_1 - C_{20} hydrocarbon group are C_1 - C_{20} alkyl groups such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, isobutyl group, t-butyl group, hexyl group and so on; C_6 - C_{20} aryl groups such as phenyl group, tolyl group, benzyl group and so on; C_1 - C_{20} alkylidene groups such as alkylaryl group or arylalkyl group, methylidene group, ethylidene group and propylidene group and so on; and C_2 - C_{20} alkenyl groups such as vinyl group and allyl group and so on. However, alkylidene groiup is excluded from R^b, R^c, R^f, and R^g. And, if either one of the R^d, R^e, R^h - R^m is an alkylidene group, the carbon atom to which that group is bound does not have other substituting group.

[0011]

Examples of the substituting groups containing halogen atoms are halogen group such as fluorine, chlorine, bromine and iodine; and halogen-substituted C_1 - C_{20} alkyl groups such as chloromethyl group, bromomethyl group, and chloroethyl group and

so on. Examples of the substituting groups containing oxygen atoms are C_1 - C_{20} alkoxy groups such as methoxy group, ethoxy group, propoxy group, and phenoxy group and so on; and C_1 - C_{20} alkoxycarbonyl groups such as methoxycarbonyl group, ethoxycarbonyl group and so on. Examples of the substituting groups having nitrogen atoms are C_1 - C_{20} alkylamino groups such as dimethylamino group, diethyl amino group, and cyano group and so on.

[0012]

Examples of the repeating units of cycloolefins represented by the general formula [Y] are norbornene, 5-methyl norbornene, 5-ethyl norbornene, 5-propyl norbornene, 5,6-dimethyl norbornene, 1-methyl norbornene, 7-methyl norbornene, 5,5,6-trimethyl norbornene, 5-phenyl norbornene, 5-benzyl norbornene, 5-ethylidene norbornene, 5-vinyl norbornene, 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydro naphthalene, 2-ethylidene-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronapahthalene, 2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 1,5-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-cyclohexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 2-isobutyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, 1,2-dihydrodicyclopentadiene, 5-chloro-norbornene, 5,5-dichcloro-norbornene, 5-fluoro-norbornene, 5,5,6-trifluoro-6-trifluoromethyl norbornene, 5-chloromethyl norbornene, 5-methoxy norbornene, 5,6-dicarboxyl norbornene anhydrate, 5-dimethylamino-norbornene, 5-cyano-norbornene and so on.

[0013]

Basically, the cycloolefin copolymer to be used in this invention is made of the above-said α-olefin component and cycloolefin component. However, beside these two essential components, other copolymerizable unsaturated monomer component(s) may be included, if necessary, as long as it does not contradict with the object of this invention. Following compounds can be mentioned as the examples of the unsaturated monomers to be copolymerized : (1) other α-oplefins than those indicated above, (2) other cycloolefins than those indicated above, (3) cyclodienes such as dicyclopentadiene and norbornadiene and so on; (4) chained dienes such as butadiene, isoprene, and 1,5-hexadiene and so on; (5) monocycloolefins such as cyclopentene and cycloheptene and so on.

[0014]

As to the cycloolefin copolymer to be used in this invention, content [x] of α-olefin unit is 80 - 99.9 mol %, preferably 85 - 99 mol %, and content [y] of cycloolefin unit is 20 - 0.5 mol %, preferably 15 - 1 mol %. And, [x] = 85 - 98 mol % and [y] = 15 - 2 mol % is particularly desirable. If the content [x] is less than 80 mol %, the copolymer will have a higher glass transition temperature (Tg) and higher tensile modulus, and as a result the copolymer and the film or sheet made of such copolymer will have insufficient elastic recovery, or poor impact resistance and elasticity. On the other hand, if the content [y] of cycloolefin unit is less than 0.5 mol %, the copolymer has a higher crystallinity and thus the effect of presence of cycloolefin component (elastic recovery) is not enough.

[0015]

Cycloolefin copolymer to be used in this invention is a preferably a substantially linear copolymer where the α-olefin unit and cycloolefin unit are arranged linearly without having a gel-like crosslinked structure. Absence of gel-like crosslinked structure can be confirmed by the complete dissolution of copolymer in decalin at 135°C. However, to be used as a stretched film, those containing a copolymer which is partially crosslinked by heat, organic peroxide or ionic radiation may be used also.

[0016]

And, limit viscosity [η] of the cycloolefin copolymer (solubility) to be used in this invention, determined in decalin at 135°C, is 0.01 - 20 dl/g. If the limit viscosity [η] is lower than 0.01 dl/g, the strength may drop significantly. And, if it exceeds 20 dl/g, moldability may turn poor. Preferred limit viscosity [η] is 0.05 - 10 dl/g.

[0017]

There is no particular restriction about the molecular weight of the cycloolefin copolymer to be used in this invention. With the soluble copolymer, the weight average molecular weight Mw (calculated as polyethylene), determined by gel permeation chromatograph (GPC), is 1,000 - 2,000,000, preferably 5,000 - 1,000,000; number average molecular weight Mn is 500 - 1,000,000 preferably 2,000 - 800,000; and molecular weight distribution (Mw/Mn) is 1.3 - 4, preferably 1.4 - 3. If the molecular weight distribution (Mw/Mn) is higher than 4, content of lower molecular compounds will increase and this may make the stretched film to become sticky.

[0018]

Glass transition temperature (Tg) of the cycloolefin copolymer to be used in this invention must not be higher than 30°C. With such copolymer, a stretched film that has excellent low temperature shrinking property can be obtained. Preferred glass transition temperature (Tg) is -30°C - 20°C, and -30°C - 15°C is particularly desirable. In this case, the glass transition temperature (Tg) can be controlled voluntarily by changing the type of monomer and composition of the cycloolefin copolymer. Thus, the glass transition temperature (Tg) can be changed voluntarily, depending on the desired application and the temperature at which it is used, and so on.

[0019]

Crystallinity of the cycloolefin copolymer to be used in this invention, determined by X-ray diffraction method, is 0 - 40%. If the crystallinity exceeds 40%, elastic recovery and transparency may decrease. Preferred crystallinity is 0 - 30%, particularly 0 - 25%.

[0020]

Tensile modulus of the cycloolefin copolymer to be used in this invention is no higher than 3,000 kg/cm^2. If the tensile modulus exceeds 3,000 kg/cm^2, an enormous energy will be needed for packing and it may be difficult to have a beautiful packages that fits the shape of the packed material when, for example, the stretched film is used as a film for packing. And, impact resistance of the stretched film may be poor. Preferred tensile modulus is 50 - 2,000 kg/cm^2.

[0021]

Preferred elastic recovery of the cycloolefin copolymer to be used in this invention is higher than 20%. If it is lower than 20%, slacking may occur or holding force may drop when an article is packed with the stretched film. Preferred elastic recovery is higher than 30%, particularly higher than 40%. Incidentally, elastic recovery is the value determined by using an autograph, at pulling speed 62 mm/minute. Thus, a test piece (width = 6 mm) was stretched by 150% between two clamps (distance L_o = 50 mm) and held for 5 minutes. Then, it was allowed to shrink without retraction, and length (L_1) of the sheet between two clamps was measured. Elastic recovery was calculated by using the following formula.

$$\text{Elastic recovery (\%)} = [1 - \{(L_1 - L_o)/L_o\}] \times 100$$

[0022]

It is desirable that the cycloolelfin copolymer to be used in this invention has a broad peak of fusion (DSC, by raising the temperature) at a temperature lower than 90°C. Copolymer having a sharp peak of fusion (DSC method, by raising the temperature) above 90°C, has a broad compositional distribution of the cycloolefin/α-olefin copolymer, and often the molded article may not have enough elastic recovery. It is desirable to have the broad peak of fusion (by DSC method) in 10 - 85°C range. In DSC (measured by raising temperature), melting point (peak of fusion) of the cycloolefin copolymer does not appear sharply. Particularly with the copolymers having a lower crystallinity, almost no peak can be detected at the level of ordinary test condition for polyethylene. And, it is desirable that the cycloolefin copolymer to be used in this invention has one ore more sub-peak(s) on the higher temperature side than the main peak obtained by DSC (measured by lowering the temperature). Due to the thermal characteristic described brefore, the stretched film has the property described above. And, the stretched film can be obtained in a more stable manner, if the range of molding temperature is wider.

[0023]

The cycloolefin copolymers to be used in this invention may be made entirely of a copolymer having its properties in the above-said range or may contain some copolymers that have its property beyond the above-said range. In the latter case, the copolymer is still acceptable as long as the overall property falls within the above-said range.

[0024]

Even though there is no particular restriction about the method with which to prepare the cycloolefin copolymer to be used in this invention, it can be prepared by copolymerizing α-olefin and cycloolefin, using the catalyst that contains the following compounds (A) and (B) as its major components or using the catalyst that contains the following compounds (A), (B) and (C) as its major components.

(A) Transition metal compounds.

(B) Compounds that can react with transition metal compound to form an ionic complex.

(C) Organoaluminium compounds.

[0025]

In this case, transition metal compounds containing the transition metal belonging to Families IVB, VB, VIB, VIIB, and VIII of the Periodic Table can be used as the above-said transition metal compound (A). Preferred transition metals are titanium, zirconium, hafnium, chromium, manganese, nickel, palladium, and platinum. Among them, zirconium, hafnium, titanium, nickel and palladium are particularly desirable.

[0026]

Even though varieties of transition metal compounds can be mentioned as such transition metal compound (A), compounds containing the transition metals belonging to Families IVB and VIIIB, in other words compounds containing a transition metal selected from Family IVB of the Periodic Table, such as titanium (Ti), zirconium (Zr) or hafnium (Hf), can be used favorably. Particularly preferred are cyclopentadienyl compound represented by the following general formula (I), (II), or (III) or their derivatives, and the compounds represented by the following general formula (IV) or their derivatives.

$$C_PM^1R^1_aR^2_bR^3_c \qquad \text{.........(I)}$$
$$C_{P2}M^1R^{1a}R^{2b} \qquad \text{........(II)}$$
$$(C_P\text{-}A_e\text{-}C_P)M^1R^1_aR^2_b \qquad \text{.......(III)}$$
$$M^1R^1_aR^2_bR^3_cR^4_d \qquad \text{........(IV)}$$

[0027]

[In the formula (I) - (IV), M^1 represents Ti, Zr or Hf atom, and C_P represents cyclic or linear unsaturated hydrocarbon groups such as chloropentadienyl group, substituted cyclopentadienyl group, indenyl group, substituted indenyl group, tetrahydroindenyl group, substituted tetrahydroindenyl group, fluorenyl group or substituted fluorenyl group. R^1, R^2, R^3, and R^4 are, respectively, ligands such as σ-bonding ligand, chelating ligand, Lewis base, and σ-bonding ligand is a hydrogen atom, oxygen atom, halogen atom, C_1 - C_{20} alkyl group, C_1 - C_{20} alkoxy group, C_6 - C_{20} aryl group, alkylaryl group or arylalkyl group, C^1 - C_{20} acyloxy group, allyl group, substituted allyl group, or substituting group containing silicon atom; and chelating ligand is acetylacetonato group, substituted acetyl-acetonato group, and so on. A represents crosslinks by covalent bonding. a, b, c and d are, respectively, integer 0 - 4, and e is an integer 0 - 6. Two or more R^1, R^2, R^3 and R^4 may bind mutually to form a ring. If C_p has a substituting group, C_1 - C_{20} alkyl group is preferred as the

substituting group. In formula (II) and (III), two C_p may be identical or different from each other.

[0028]

Examples of the substituted cyclopentadienyl group in the above-said formula (I) - (III) are methylcyclopentadienyl group, ethylcyclopentadienyl group, isopropylcyclopentadienyl group, 1,2-dimethylcyclopentadienyl group, tetramethylcyclopentadienyl group, 1,3-dimethylcyclopentadiethyl group, 1,2,3-trimethylcyclopentadienyl group, 1,2,4-trimethylcyclopentadienyl group, pentamethylcyclopentadienyl group, trimethylsilylcyclopentadienyl group and so on. Examples of R^1 - R^4 are halogen atoms such as fluorine atom, chlorine atom, bromine atom, iodine atom; C_1 - C_{20} alkyl groups such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, octyl group, and 2-ethylhexyl group; C_1 - C_{20} alkoxy groups such as methoxy group, ethoxy group, propoxy group, buthoxy group, and phenoxy group; C_6 - C_{20} aryl groups, allylalkyl groups, and allylaryl group such as phenyl group, tolyl group, xylyl group, and benzyl group; C_1 - C_{20} acyloxy groups such as heptadecylcarbonyloxy group; substituting groups containing silicon atom such as trimethylsilyl group and (trimethylsilyl)methyl group; Lewis base such as ethers (dimethyl ether, diethyl ether, tetrahydrofuran and so on), thioethers (tetrahydrothiophene and so on), esters (ethyl benzoate and so on), nitriles (acetonitrile, benzonitrile and so on), amines (trimethylamine, triethylamine, tributylamine, N,N-dimethyl aniline, pyridine, 2,2'-bipyridine, phenanthroline, and so on), and phosphines (triethyl phosphine, and triphenyl phosphine and so on); linear unsaturated hydrocarbons such as ethylene, butadiene, 1-pentene, isoprene, pentadiene, 1-hexene and their derivatives; cyclic unsaturated hydrocarbons such as benzene, toluene, xylene, cycloheptatriene, cyclooctadiene, cyclooctatriene, cyclooctatetraene, and their derivatives. Examples of the covalented crosslinkage of A are methylene crosslinkage, dimethylmethylene crosslinkage, ethylenic crosslinkage, dimethylsilylene crosslinkage, dimethyl germylene (SIC) crosslinkage, and dimethylstanylene (SIC) crosslinkage and so on.

[0029]

Following compounds and the following compounds whose zirconium has been substituted by titanium or hafnium can be mentioned as the examples of such compounds.

Compounds of formula (I)

(Pentamethylcyclopentadiethyl)trimethyl zirconium, (pentamethylcyclopentadienyl) triphenyl zirconium, (pentamethylcyclopentadienyl) tribenzyl zirconium, (pentamethyl cyclopentadienyl) trichloro zirconium, (pentamethylcyclopentadienyl) trimethoxy zirconium, (cyclopentadienyl) trimethyl zirconium, (cyclopentadienyl) triphenyl zirconium, (cyclopentadienyl) tribenzyl zirconium, (cyclopentadienyl) trichloro zirconium, (cyclopentadienyl) trimethoxy zirconium, (cyclopentadienyl) dimethyl-(methoxy) zirconium, (methylcyclo-pentadienyl) trimethyl zirconium, (methylcyclo-pentadienyl) triphenyl zirconium, (methylcyclopentadienyl) trichloro zirconium, (methylcyclopentadienyl) dimethyl(methoxy) zirconium, (dimethylcyclo-pentadienyl) trichloro zirconium, (trimethylcyclopentadienyl) trichloro zirconium, (trimethyl-silylcyclopentadienyl) trimethyl zirconium, (tetramethylcyclopentadienyl) trichloro zirconium.

[0030]

Compounds of formula (II)

BIS(cyclopentadienyl) dimethyl zirconium, BIS(cyclopentadienyl) diphenyl zirconium, BIS(cyclopentadienyl) diethyl zirconium, BIS(cyclopentadienyl) dibenzyl zirconium, BIS(cyclopentadienyl dimethoxy zirconium, BIS(cyclopentadienyl) dichloro zirconium, BIS(cyclopentadienyl) dihydrido zirconium, BIS(cyclopentadienyl) monochloromonohydrido zirconium, BIS(methylcyclopentadienyl) dimethyl zirconium, BIS(methylcyclopentadienyl) dichloro zirconium, BIS(methylcyclopentadienyl) dibenzyl zirconium, BIS(pentamethylcyclopentadienyl) dimethyl zirconium, BIS(pentamethyl-cyclopentadienyl) dichloro zirconium, BIS(pentamethylcyclopentadienyl) dibenzyl zirconium, BIS(pentamethylcyclopentadietnyl) chloromethyl zirconium, BIS(penta-methylcyclopentadienyl) hydridomethyl zirconium, (cyclopentadienyl)(pentamethyl-cyclopentadienyl) dichloro zirconium.

[0031]

Compounds of formula (III)

Ethylene BIS(indenyl) dimethyl zirconium, ethylene BIS(indenyl)dichloro zirconium, ethylene BIS(tetrahydroindenyl) dimethyl zirconium, ethylene BIS(tetra-hydroindenyl)dimethyl zirconium, ethylene BIS(tetrahydroindenyl)dichloro zirconium, dimethylsilylene BIS(cyclopentadienyl)dimethyl zirconium, dimethylsilylene BIS(cyclopentadienyl)dichloro zirconium, isopropyl(cyclopentadienyl)(9-fluorenyl) dimethyl zirconium, isopropyl(cyclopentadienyl)(9-fluorenyl)dichloro zirconium,

[phenyl(methyl)methylene](9-fluorenyl)(cyclopentadienyl)dimethyl zirconium, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)dimethyl zirconium, ethylidene-(9-fluorenyl)(cyclopentadienyl)dimethyl zirconium, cyclohexyl(9-fluorenyl)(cyclopentadienyl)dimethyl zirconium, cyclopentyl(9-fluorenyl)(cyclopentadienyl)dimethyl zirconium, cyclobutyl(9-fluorenyl)(cyclopentadienyl)dimethyl zirconium, dimethylsilylene(9-fluorenyl)(cyclopentadienyl)dimethyl zirconium, dimethylsilylene BIS-(2,3,5-trimethylcyclopentadienyl)dichloro zirconium, dimethylsilylene BIS(2,3,5-trimethylcyclopentadienyl)dimethyl zirconium.

[0032]

Compounds represented by the afore-said formula (IV) can be mentioned as the example of the compounds other than the cyclopentadienyl compounds represented by the general formula (I), (II), and (III). Examples are zirconium compounds, hafnium compounds and titanium compounds having one, two or more alkyl groups, alkoxy groups or halogen atoms, such as the following compounds, or the following compounds where the zirconium has been replaced by hafnium or titanium, such as tetramethyl zirconium, tetrabenzyl zirconium, tetramethoxy zirconium, tetraethoxy zirconium, tetrabutoxy zirconium, tetraphenoxy zirconium, tetra(2-ethylhexyloxy) zirconium, tetrachloro zirconium, tetrabromo zirconium, butoxytrichloro zirconium, dibutoxydichloro zirconium, BIS(2,6-di-t-butylphenoxy)dimethyl zirconium, BIS(2,6-di-t-butylphenoxy)dichloro zirconium, zirconium TETRAKIS(acetylacetonate).

[0033]

There is no particular restriction about the transition metal compounds that contain the transition metals of Families VB - VIII. Examples of chromium compound are tetramethyl chromium, tetra(t-butoxy) chromium, BIS(cyclopentadienyl) chromium, hydridotricarbonyl (cyclpentadienyl) chromium, hexacarbonyl (cyclopentadiethyl) chromium, hexacarbonyl (cyclopentadienyl) chromium, BIS(benzene) chromium, tricarbonyl TRIS(triphenyl phosphonato) chromium, TRIS(allyl) chromium, triphenyl TRIS(tetrahydrofuran) chromium, and chromium TRIS(acetylacetonate) and so on.

[0034]

Examples of manganese compound are tricarbonyl (cyclopentadienyl) manganese, pentacarbonylmethyl manganese, BIS(cyclopentadienyl) manganese, manganese BIS(acetylacetonate) and so on.

[0035]

Examples of nickel compound are dicarbonyl BIS(triphenylphosphine) nickel, dibromo-BIS(triphenylphosphine) nickel, dinitrogeno-BIS(BIS(tricyclohexylphosphine) nickel), chlorohydrido-BIS(tricyclohexylphosphine) nickel, chloro-(phenyl) BIS(triphenylphosphine) nickel, dimethyl-BIS(trimethylphosphine) nickl, diethyl(1,1'-bipyridyl) nickel, BIS(allyl) nickel, BIS(cyclopentadienyl) nickel, BIS(methylcyclopentadienyl) nickel, BIS(pentamethylcyclopentadienyl) nickel, allyl(cyclopentadienyl) nickel, (cyclopentadienyl)(cyclooctadiene) nickel tetrafluoroborate salt, BIS(cyclooctadiene) nickel, nickel BIS-acetylacetonate, allyl nickel chloride, TETRAKIS(triphenylphosphine) nickel, nickel chloride, $(C_6H_5)Ni[OC(C_6H_5)CH=P(C_6H_5)_2][P(C_6H_5)_3]$, $(C_6H_5)Ni\{OC(C_6H_5)C(SO_3Na)=P(C_6H_5)_2\}\{P(C_6H_5)_3\}$ and so on.

[0036]

Examples of palladium compound are dichloro-BIS(benzonitrile) palladium, carbonyl-TRIS(triphenylphosphine) palladium, dichloro-BIS(triethylphosphine) palladium, BIS(isocyanated t-butyl) palladium, palladium BIS(acetylacetonate), dichloro-(tetraphenylcyclobutadiene) palladium, dichloro-(1,5-cyclooctadiene) palladium, BIS(allyl) palladium, allyl (1,5-cyclooctadiene) palladium tetrafluoroborate salt, (acetylacetonato)(1,5-cyclooctadiene) palladium tetrafluoroborate salt, TETRAKIS(acetonitrile) palladium bitetrafluoroborate salt and so on.

[0037]

Any compounds that can react with the transition metal compound (A) to form an ionic complex can be used as the compound (B). And, compounds made from cation and an anion that has a plurality of groups bound to the element, particularly the ligand complex compound made from a cation and an anion that has a plurality of groups bound to the element can be used favorably. Compounds represented by the following formula (V) or (VI) can be used appropriately as the compounds made from a cation and an anion that has a plurality of groups bound to the element.

$$[(L^1 - R^7)^{k+}]_p[(M^3Z^1Z^2.....Z^n)^{(n-m)-}]_q \qquad ....(V)$$

$$[(L^2)^{k+}]_p[(M^4Z^1Z^2.....Z^n)^{(n-m)-}]_q \qquad ...(VI)$$

[where, L^2 represents M^5, $R^8R^9M^6$, $R^{10}{}_3C$ or $R^{11}M^6$]

[0038]

[In the formula (V) and (VI), L^1 is a Lewis base; M^3 and M^4 are, respectively, the elements selected from Families VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA and VA of the Periodic Table; M^5 and M^6 are, respectively, the element selected from the Families IIB, IVB, VB, VIB, VIIB, VIII, IA, IB, IIA, IIB and VIIA of the Periodic Table; Z^1 - Z^n are, respectively, hydrogen atoms, dialkylamino group, C_1 - C_{20} alkoxy group, C_6 - C_{20} aryloxy group, C_1 - C_{20} alkyl group, C_6 - C_{20} aryl group, alkylaryl group and arylalkyl group, C_1 - C_{20} halogen-substituted hydrocarbon group, C_1 - C_{20} acyloxy group, organometaloid group or halogen atom; and two of the Z^1 - Z^n may be bound together to form a ring. R^7 is a hydrogen atom, C_1 - C_{20} alkyl group, C_6 - C_{20} aryl group, alkylaryl group or arylalkyl group; R^8 - R^9 are, respectively, cyclopentadienyl group, substituted cyclopentadienyl group, indenyl group or fluorenyl group; and R^{10} is a C_1 - C_{20} alkyl group, aryl group, alkylaryl group or arylalkyl group. R^{11} represents a large cyclic ligand such as tetraphenyl porphyrin or phthalocyanin and so on. m is the atomic valency of M^3 and M^4 and is an integer 1 - 7; n is an integer 2 - 8; k is the ionic valency of (L^1 - R^7) and (L^2) and is an integer 1 - 7; p is an integer of 1 or more; and q is (p x k)/(n - m)].

[0039]

Examples of Lewis base are ammonia; amines such as methylamine, aniline, dimethylamine, diethylamine, N-methyl aniline, diphenylamine, trimethylamine, triethylamine, tri-n-butylamine, N,N-dimethyl aniline, methyldiphenylamine, pyridine, p-bromo-N,N-dimethyl aniline, and p-nitro-N,N-dimethyl aniline and so on; phosphines such as triethyl phosphine, triphenyl phosphine, diphenyl phosphine and so on; ethers such as dimethyl ether, diethyl ether, tetrahydrofuran, dioxane and so on; thioethers such as diethyl thioether and tetrahydrothiophene and so on; and esters such as ethyl benzoate and so on. Examples of M^3 and M^4 are B, Al, Si, P, As, and Sb, preferably B or P; examples of M^5 are Li, Na, Ag, Cu, Br, I and I_3; and examples of M^6 are Mn, Fe, Co, Ni, and Zn.

[0040]

Examples of Z^1 - Z^n are dialkylamino group such as dimethylamino group and diethylamino group; C_1 - C_{20} alkoxy group such as methoxy group, ethoxy group, and n-butoxy group; C_6 - C_{20} aryloxy group such as phenoxy group, 2,6-dimethylphenoxy group, and naphthyloxy group; C_1 - C_{20} alkyl group such as methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, n-octyl group, and 2-ethylhexyl group; C_6 - C_{20} aryl group, alkylaryl group or arylalkyl group such as phenyl group, p-tolyl

group, benzyl group, 4-t-butylphenyl group, 2,6-dimethylphenyl group, and 2,3-dimethylphenyl group; C_1 - C_{20} halogen-substituted hydrocarbon group such as p-fluorophenyl group, 3,5-difluorophenyl group, pentachlorophenyl group, 3,4,5-trifluorophenyl group, pentafluorophenyl group, and 3,5-di(trifluoromethyl)phenyl group; halogen atoms such as F, Cl, Br, and I; organometaloid group such as pentamethyl antimony group, trimethylsilyl group, trimethyl germyl group, diphenylalcyne (SIC) group, dicyclohexyl antimony group, and diphenyl boron group and so on. Compounds described above can be mentioned as the examples of R^7 and R^{10}. Examples of substituted cyclopentadienyl group (R^8 and R^9) are alkyl group-substituted cyclopentadienyl groups such as methylcyclopentadienyl group, butylcyclopentadienyl group, and pentamethylcyclo-pentadienyl group and so on. Here, number of carbons in the alkyl group is normally 1 - 6, and the number of alkyl substituting groups can be selected from 1 - 5. Among the compounds represented by formula (V) and (VI), those which have boron as the M^3 and M^4 are preferred.

[0041]

Among the compounds represented by the formula (V) and (VI), following compounds can be used appropriately.

Compounds of formula (V)

Tetraphenyl borate triethyl ammonium, tetraphenyl borate tri(n-butyl) ammonium, tetraphenyl borate trimethyl ammonium, tetraphenyl borate tetraethyl ammonium, tetraphenylborate methyl tri(n-butyl) ammonium, tetraphenyl borate benzyl tri(n-butyl) ammonium, tetraphenyl borate dimethyldiphenyl ammonium, tetraphenyl borate triphenyl ammonium, tetraphenyl borate trimethyl anilinium, tetraphenyl borate methyl pyridinium, tetraphenyl borate benzyl pyridinium, tetraphenyl borate methyl(2-cyano-pyridinium), tetraphenyl borate trimethyl sulfonium, tetrapahenyl borate benzyl dimethyl sulfonium.

[0042]

TETRAKIS(pentafluorophenyl) borate triethyl ammonium, TETRAKIS-(pentafluorophenyl) borate tri(n-butyl) ammoniumm, TETRAKIS(pentafluorophenyl) borate triphenyl ammonium, TETRAKIS(pentafluorophenyl) borate tetrabutyl ammonium, TETRAKIS(pentafluorophenyl) borate (tetraethyl ammonium), TETRAKIS-(pentafluorophenyl) borate [methyltri(n-butyl) ammonium], TETRAKIS(pentafluorophenyl) borate [benzyltri(n-butyl) ammonium], TETRAKIS(pentafluorophenyl) borate methyldiphenyl ammonium, TETRAKIS(penta-fluorophenyl) borate methyl-

triphenyl ammonium, TETRAKIS(pentafluorophenyl) borate dimethyldiphenyl ammonium, TETRAKIS(pentafluorophenyl) borate anilinium, TETRAKIS(pentafluorophenyl) borate methyl anilinium, TETRAKIS(pentafluorophenyl) borate dimethyl anilinium, TETRAKAIS(pentafluorophenyl) borate trimethyl anilinium, TETRAKIS-(pentafluoro-phenyl) borate dimethyl(m-nitroanilinium), TETRAKIS-(pentafluoro- phenyl) borate dimethyl(p-bromo anilinium).

[0043]

TETRAKIS(pentafluorophenyl) borate pyridinium, TETRAKIS(pentafluorophenyl) boron (p-cyanopyridinium), TETRAKIS(pentafluorophenyl) borate (N-methyl-pyridinium), TETRAKIS(pentafluorophenyl) borate (N-benzyl pyridinium), TETRAKIS-(pentafluorophenyl) borate (O-cyano-N-methyl pyridinium), TETRAKIS-(pentafluoro-phenyl) borate (p-cyano-N-methyl pyridinium), TETRAKIS(pentafluorophenyl) borate (p-cyano-N-benzyl pyridinium), TETRAKIS(pentafluoro-phenyl) borate trimethyl sulfonium, TETRAKIS-(pentafluorophenyl) borate benzyldimethyl sulfonium, TETRAKIS(pentafluorophenyl) borate tetraphenyl phosphonium, tetra(3,5-ditrifluoromethylphenyl) borate dimethyl anilinium, and hexafluoroarsenate triethyl ammonium.

[0044]

Compounds of formula (VI)

Tetraphenyl borate ferrosenium, tetraphenyl borate silver, tetraphenyl borate tolytyl (SIC), tetraphenyl borate (tetraphenyl porphyrin manganese), TETRAKIS-(penta-fluorophenyl) borate ferrosenium, TETRAKIS(pentfluorophenyl) borate decamethyl ferrosenium, TETRAKIS(pentafluorophenyl) borate acetyl ferrosenium, TETRAKIS(pentafluorophenyl) borate formyl ferrosenium, TETRAKIS(pentafluoro-phenyl) borate cyanoferrosenium, TETRAKIS(pentafluorophenyl) borate silver, TETRAKIS(pentafluoro-phenyl) borate tolytyl (SIC), tetrakis(pentafluorophenyl) borate lithium, TETRAKIS(pentafluorophenyl) borate lithium, TETRAKIS(pentafluorophenyl) borate sodium, TETRAKIS(pentafluorophenyl) borate (tetraphenyl-porphyrin manganese), TETRAKIS(pentafluorophenyl) borate (tetra-phenylporphyrin iron chloride), TETRAKIS(pentafluorophenyl) borate (tetraphenyl porphyrin zinc), tetrafluoro-borate silver, hexafluoro-arsenate silver, hexafluoro-antimonate silver.

[0045]

And, compounds other than those illustrated in the formula (V) and (VI, such as tri(pentafluorophenyl)boron, tri[3,5-di(trifluoromethyl)phenyl] boron, or triphenyl boron may be used also.

[0046]

Compounds represented by the following general formula (VII), (VIII) or (IX) can be mentioned as the organoaluminium compound [component (C)].

$$R^{12}{}_{r}AlQ_{3-r} \qquad \ldots(VII)$$

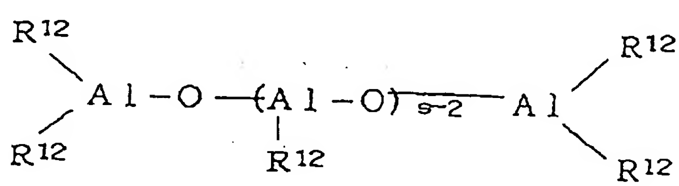
[R^{12} is a C_1 - C_{20}, preferably C_1 - C_{12}, hydrocarbon group such as alkyl group, alkenyl group, aryl group, or arylalkyl group; Q is a hydrogen atom, halogen atom or C_1 - C_{20} alkoxy group. r is $1 \leqq r \leqq 3$]

Examples of the compounds represented by formula (VII) are trimethyl aluminium, triethyl aluminium, triisobutyl aluminium, dimethyl aluminium chloride, diethyl aluminium chloride, methyl aluminium dichloride, ethyl aluminium dichloride, dimethyl aluminium fluoride, diisobutyl aluminium hydride, diethyl aluminium hydride, ethyl aluminium sesqui-chloride, and so on.

[0047]

Linear aluminoxane represented by the following formula (VIII).

[Formula 3]



··· (VIII)

[where, R^{12} represents the same as in formula (VII). s represents the degree of polymerization, and is normally 3 - 50, preferably 7 - 40]

[0048]

Cycloalkyl aluminoxane having a repeating unit represented by the following formula (IX).

[Chemical formula 4]

$$-\!\!\left(\underset{\displaystyle R^{12}}{\underset{|}{\mathrm{Al}}}-\mathrm{O}\right)_{s}\!\!- \qquad \cdots \text{ (IX)}$$

[where, R^{12} represents the same as in formula (VII).
s represents the degree of polymerization, and is
normally 3 - 50, preferably 7 - 40]

Preferred among the compounds represented by formula (VII) - (IX) are alkyl groups having 3 or more carbons, and aluminoxanes or alkyl group-containing aluminium compound having at least 1 or more branched alkyl group are particularly desirable. And, even more desirable is triisobutyl aluminium or the aluminoxane having 7 or higher degree of polymerization. If triisobutyl aluminium or aluminoxane having 7 or more degree of polymerization or their mixture is used, high activity can be achieved. And, modified aluminoxane prepared by modifying the aluminoxane represented by the formula (VII) - (IX) with a compound having an active hydrogen such as water, can be used favorably.

[0049]

A method of contacting the alkyl aluminium with a condensing agent such as water can be mentioned as a method for preparation of the aluminoxane, but there is no particular restriction, and any known method can be used for the reaction. For example, (1) a method by which organoaluminium compound is dissolved in an organic solvent and this solution is contacted with water, (2) a method by which organoaluminium compound is added initially at the time of polymerization, and then water is added later, (3) a method by which the crystalline water contained in the metal salt, or the water adsorbed on the inorganic or organic substance is reacted with organoaluminium compound, or (4) a method by which trialkyl aluminium is reacted with tetralkyldialumioxane and then the reaction mixture is reacted further with water, are available.

[0050]

The catalyst to be used for preparation of the olefin copolymer of this invention contains the components (A) and (B) or components (A), (B), and (C) as its major components. In this case, there is no restriction about the condition as to how to use the component (A) and component (B), but it is desirable to set the mol ratio of the

component (A) and component (B) to 1 : 0.01 - 1 : 100, preferably 1 : 0.5 - 1 : 10, and particularly 1 : 1 - 1 : 5. And, it is desirable to use the temperature from -100 - 250°C range, and the pressure and time can be set volantarily.

[0051]

And, the amount of component (C) to use is normaly 0 - 2,000 mols, preferably 5 - 1,000 mols, and particularly 10 - 500 mols, per mole of component (A). If component (C) is used, polymerization activity can be improved. However, exccessive use of component (C) may leave behind a large amount of organoaluminium compound in the polymer, which is not desirable.

[0052]

There is no particular restriction about how to use the catalyst component. For example, component (A) and component (B) may be pre-contacted or the product from contact may be separated, washed and used, or the components may be contacted and used in the polymerization system. And, components (C) may be contacted ahead of time with the component (A) or component (B), or the product from contact of component (A) and component (B). And, catalyst components may be added ahead of time to monomer or polymerization solvent, or may be added in the polymerization system. And, catalyst components, if necessary, may be supported on an inorganic or organic carrier for use.

[0053]

The amount, relative to the feedstock, of catalyst to use is feedstock monomers/ component (A) (mol ratio) = 1 - 10^9, preferably 100 - 10^7.

[0054]

Any one of the bulk polymerization process, solution polymerization process, suspension polymerization process, or vapor-phase polymeriation process can be used as the polymerization process. And, it may be a batch process or a continuous process. In case of using a polymerization solvent, aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenene, and so on; alicyclic hydrocarbons such as cyclopentane, cyclohexane, methylcyclohexane and so on; aliphatic hydrocarbons such as pentane, hexane, heptane, octane and so on; and halogenated hydrocarbons such as chloroform, dichloromethane and so on may be used. These solvents may be used alone, or as a mixture of two or more. And, monomers such as α-olefin may be used as the solvent.

[0055]

As to the polymerization condition, the polymerization temperature is -100 - 250°C, preferably -50 - 200°C. Polymerization time is normally 1 minute - 10 hours, reaction pressure is from normal pressure to 100 kg/cm^2, preferably from normal pressure to 50 kg/cm^2. Molecular weight of the copolymer can be regulated by selecting the amount of each catalyst component or polymerization temperature, or by running the polymerization reaction in the presence of hydrogen.

[0056]

The stretched film of this invention is made by monoaxially or biaxially drawing (stretching) the film stock (sheet or film) made of the afore-said cycloolefin copolymer. In this case, the stretched film of this invention is formed, preferably, by stretching the film stock in longitudinal (MD) direction by 0 - 20 folds and stretching in transverse (TD) direction by 0 - 20 folds.

[0057]

As to the method of forming the film stock (sheet or film), method of molding ordinary sheet or film, such as T-die process or inflation process can be employed. In this case, even though there is no particular restriction about the thickness of the film stock, the thickness is normally 0.01 - 5mm, preferably 0.02 - 3 mm. And, various additives or fillers may be added to the cycloolefin copolymer that forms the film stock (sheet or film). Heat resistant stabilizer, weatherability stabilizer, antistatic, slipping agent, anti-blocking agent, anti-fogging agent, lubricant, foaming agent, dye, pigment, natural oil, synthetic oil, wax, and so on can be mentioned as the examples of additives, and its amounts can be selected appropriately. Stretched film of this invention with excellent low temperature shrinking property can be obtained by stretching the formed film stock in longitudinal (MD) direction by 0 - 20 folds and in transverse (TD) direction by 0 - 20 folds.

[0058]

Stretching (drawing) is carried out monoaxially, sequentially or simultaneously in longitudinal and/or transverse direction, at a stretching temperature (higher than the glass transition temperature (Tg) of the cycloolefin copolymer, but lower than its softening point). Draw ratio in MD and/or TD direction can be selected voluntarily, depending on the targeted property. In this case, there is no particular restriction about the stretching temperature that can be used to prepare the stretched film of this invention, and the temperature is normally Tg + 30°C - Tg + 150°C, preferably

Tg + 40°C - Tg + 100°C. If the film stock made of the cycloolefin copolymer is stretched in Tg - Tg + 60°C range or Tg + 40°C range (stretching temperature used for ordinary resin), elastic recovery after stretching will be greater, and thus the resin can not be drawn thoroughly. Ordinary drawing method such as roll drawing method, tenter drawing method, inflation process, etc. can be employed.

[0059]

Preferred method for preparation of the stretched film of this invention is explained embodically in the following. First, a film stock or a sheet stock having a thickness of 0.011 - 5 mm, preferably 0.02 - 3 mm is formed from the cycloolefin copolymer by T-die molding process or inflation molding process, etc.. Then, this film stock is stretched (drawn) monoaxially or sequentially or simultaneously in longitudinal and/or transverse direction at the stretching temperature described above.

[0060]

Because the stretched film of this invention has a low temperature shrinking property, it can be regulated simply to any desired shape. For example, the stretched film of this invention can be used effectively as a packing material for foods, medical products, and for shipment. In this case, the stretched film of this invention has excellent transparency, and has enough strength to protect the packed material from external force, such as shock, vibration, pressure, which prevails during the flow and distribution process. Incidentally, there is no particular restriction about the thickness of the stretched film of this invention, and the stretched film of this invention includes also the sheets.

[0061]

[Examples]

This invention is explained further by way of the following comparative examples and examples which, however, are not intended to limit the scope of this invention. Prior to manufacture of laminated material, cycloolefin copolymers (Reference Examples 1 and 2) were prepared.

[0062]

<u>Reference Example 1</u> [Copolymerization of ethylene and 2-norbornene]

Toluene 15 liters, triisobutyl aluminium (TIBA) 23 mmols, zirconium tetrachloride 0.038 millimol, tetra(pentafluorophenyl) borate anilinium 0.060 millimol were added in that order in a 30 liter autoclave at room temperature in nitrogen gas atmosphere,

and then a toluene solution 2.4 liters containing 2-norbornene 70 weight % (16.0 mols, as 2-norbornene) was added. After raising the temperature to 80°C, ethylene gas was introduced continuously while maintaining the ethylene partial pressure at 8 kg/cm^2, to run the reaction for 110 minutes. After completing the reaction, the polymer solution was poured in methanol 15 liters to preciptiate the polymer. This precipitated polymer was collected by filtration and dried, to obtain a cycloolefin copolymer (a1). Yield of the cycloolefin copolymer (a1) was 2.93 kg. Polymerization activity was 846 kg/g Zr.

[0063]

The thus-obtained cycloolefin copolymer (a1) gave the following properties. The content of norbornene, determined from the ratio of the sum of the peak of methylene group near 30 ppm in ^{13}C-NMR spectra and the peak of methylene at 5- and 6-position of norbornene, and the peak of methylene group at 7-position of norbornene near 32.5 ppm, was 7.7 mol %. Limit viscosity [η], determined at 135°C in decalin, was 1.01 dl/g, and crystallinity, determined by X-ray diffraction method, was 1.0%. Using a Vibron Model 11-EA (manufactured by Toyo Bolding K.K.), a test piece (width = 4 mm, length = 40 mm, thickness = 0.1 mm) was tested at a frequency = 3.5 Hz and rate of temperature elevation = 3°C/minute. From the peak of loss modulus (E") determined under this condition, glass transition temperature (Tg) was calculated. Tg was 0°C. Using ALC/GPC 150C (manufactured by Waters Co.), molecular weights and molecular weight distribution were determined. Weight average molecular weight Mw (calculated as polyethylene) was 58,100, number average Mn was 30,400, and molecular weight distribution Mw/Mn was 1.91. When the melting point (Tm) was measured in - 50°C - 150°C range by DSC (Perkin-Elmers Series 7 DSC, rate of elevation of temperature = 10°C/minute), Tm was 72°C (a broad peak).

[0064]

Reference Example 2 [Copolymerization of ethylene and 2-norbornene]

Procedure of Reference Example 1 was repeated, except changing the triisobutyl aluminium to ethyl aluminium sesqui-chloride 300 millimols, zirconium tetrachloride to $VO(OC_2H_5)Cl_2$ 30 millimols, omitting the tetra(pentafluorophenyl) borate anilinium, changing the amount of 2-norbotrnene to 3 mols, the polymerization temperature to 30°C, ethylene partial pressure to 1 kg/cm^2, and polymerization time to 30 minutes, to obtain a cycloolefin copolymer (a2). Yield of cycloolefin copolymer (a2) was 480 g. Norbornene content was 24.6 mol %, limit viscosity [η] was 1.21 dl/g, melting

point (Tm) was 100°C (a sharp peak), glass transition temperature (Tg) was 50°C, and Mw/Mn was 4.26.

[0065]

Examples that have employed the cycloolefin copolymers obtained in the above-described Reference Examples, and comparative examples are presented in the following.

<u>Examples 1 - 7 and Comparative Examples 1 - 2</u>

Cycloolefin copolymers (a1) and (a2) were heat-pressed at 190°C and 100 kg/cm^2 for 3 minutes, to obtain a film stock having a thickness of 100 µm. A test piece having a length = 20 mm and width = 100 mm was cut from this film stock, and it was stretched monoaxially at the stretching temperature and stretching ratio (draw ratio) shown in the following table, and it was held there for 1 minute, and then cooled. Stretching ratio of the test piece after releasing the tension and dynamic properties of the stretched film were measured, and results are presented in the following table.

[0066]

Each property was tested in the following manner.

Tensile modulus : Pprocedure specified in JIS K-7113 was followed, using the Autograph.

Tensile fracture strength : Procedure specified in JIS K-7113 was followed, using the Autograph.

Tensile fracture elongation : Procedure specified in JIS K-7113 was followed, using the Autograph.

Elastic recovery : Autograph was used. A test piece [width = 6 mm, distance between clamps = 50 mm (L_o)] was pulled by 150% at a pulling speed of 62 mm/minute, and then kept in that condition for 5 minutes. Then, the test piece was allowed to shrink abruptly without retraction. Length (L_1) of the sheet between the clamps was measured after 1 minute, and elastic recovery was calculated by the following formula.

$$\text{Elastic recovery (\%)} = [1 - \{(L_1 - L_o)/L_o\}] \times 100$$

In this case, acceptable elastic recovery is higher than 10%, particularly higher than 30%. And, higher than 60% is even more desirable.

Haze : Using Digital Haze Computer (manufactured by Suga Shikenki K.K.), test was conducted by the procedure specified in JIS K-7105.

Thermal shrinkage ratio : A test piece (width = 6 mm, length = 40 mm) was soaked in warm water (60°C and 70°C) for 5 seconds, and then the length L_2 (mm) was measured. Shrinkage ratio (%) was calculated by the following formula.

$$\text{Thermal shrinkage ratio (\%)} = [1 - (L_2/40)] \times 100$$

[0067]
[Table 1]
Table 1 is presented in the next page.

[0068]
[Effect of invention]
As explained above, the stretched film of this invention excels in transparency, low temperature shrinking property and elastic recovery, and has an improved tensile fracture strength and elastic recovery ratio.

[Table 1]

		Copolymer	Stretching temperature (°C)	Stretching ratio	Relaxation ratio *1	Tensile modulus (kg/cm^2)	Strength at fracture (kg/cm^2)	Elongation at fracture (%)	Elastic recovery (%)	Thermal shrinkage ratio *2 (%) 60°C	Thermal shrinkage ratio *2 (%) 70°C	Haze (%)
Examples	1	a 1	70	4	4	980	325	266	95	15	25	1.4
	2	a 1	70	6	6	1055	410	236	93	19	30	1.3
	3	a 1	70	10	10	1500	425	131	90	25	28	1.5
	4	a 1	60	4	3	825	575	147	98	45	55	1.2
	5	a 1	60	6	3.7	825	725	124	99	50	57	1.3
	6	a 1	50	4	2.5	635	415	167	100	47	55	1.5
	7	a 1	50	6	3.1	890	920	136	100	50	60	1.3
Comp. Examples	1	a 1	—	—	—	685	280	391	95	0	0	1.4
	2	a 2	90	4	4	26000	610	4	Fractured	0	0	4.5

*1 : Actual shinkage ratio after the shrinkage when it was relaxed from tension after stretching at the temperature and stretching ratio indicated in the text.
*2 : Shrinkage ratio, after soaking in warm water for 5 seconds.